Quantitative Determination of Carbon and Nitrogen Using the Electron Microprobe

NIST participated in an international round-robin exercise on the quantitative determination of carbon and nitrogen. The exercise was conducted by CCQM (Comité consultatif pour la quantité de matière – métrologie en chimie) a committee of the BIPM (Bureau International des Poids et Mesures) and included primarily National Metrology Institutes (NMIs). The three samples measured were two films (2 μm to 3 μm thick) of Vanadium-Nitride and Titanium-Carbide and a bulk steel containing carbon. Carbon and nitrogen are two low atomic number elements that are difficult to analyze with the electron microprobe. The goals of this project were not only to provide CCQM with the data for their round robin, but also to develop new analytical protocols and standards to improve our ability to analyze light elements.

R. Marinenko and S. Wight (Div. 837)

CCQM (English title: Consultative Committee for Amount of Substance – Metrology in Chemistry) provided the two specimens of 2 μm to 3 μm thick films of TiC and VN on stainless steel. The analysis technique, experimental parameters, and quantification data reduction procedures were optional. We chose to use wavelength dispersive electron probe microanalysis (WDS-EPMA). The other seven laboratories used EPMA with the exception of one that used X-ray photoelectron spectroscopy (XPS). Carbon and Nitrogen are difficult to analyze by EPMA for several reasons: 1) Kα x-rays of both elements are readily absorbed by the matrix, especially by heavier elements; 2) x-ray spectral peaks for both C and N are broad and shift with the bonding environment of the element; 3) stoichiometric reference standards are not readily available.

The most difficult aspect of this project was the search for and characterization of reference standards for the analysis. Fortunately, we were able to obtain three TiC specimens as well as a commercial powder of VN that had particles in the 8 μm to 10 μm diameter range, large enough for analysis with the electron probe without sampling areas outside of the particles. We tested these specimens for microheterogeneity and quantified them with pure elemental Ti and V standards. We determined that one of the TiC specimens, a single-crystal, and the VN particle specimen was stoichiometric. This was fortunate since TiC has a complex phase diagram and often occurs in a sub-stoichiometric form with vacancies in the sublattice.

Securing reference standards similar to the films being analyzed enabled us to use peak height measurements for quantification as no peak shifts between the standard and unknown were observed.

The films were thick enough to be treated as bulk specimens (confirmed by consistencies in our data and by Monte Carlo calculations) and were analyzed at multiple excitation potentials, 7.5 keV, 10 keV, 12.5 keV, and 15 keV, all at a current of 50 nA. We used synthetic multilayered crystals, LDEC for C and OV080 for N. For Ti and V we used a PET crystal. Fifty points were analyzed for each film. Our results from the four voltages had an uncertainty (a single standard deviation) of 1 % relative for both C and N. A small uncertainty between the results of the different voltages is used to validate the data reduction procedure which corrects for other elements present in the matrix. Our data reduction software, Probe for Windows (PFW) can test binary compound data using all available correction procedures with as many as five different mass absorption coefficient tables to determine which combinations are the most accurate. With this help we chose the Armstrong/Love-Scott with LINEMU MACs to quantify the raw data for the quantification of both the reference standards and the films.

In the table below, our results are compared to the range of values reported in the first round of reported by CCQM. The range of values probably reflects the differences in excitation potentials, data collection and processing. Our results for C in TiC are at the lower end of the range but there are four other laboratories' results, including the one using XPS with values only 1% to 2 % mass fraction higher than the NIST result. This low value for C in TiC also reflects the fact that there is no mass balance for us and the four other laboratories. Some of the other participating laboratories may not know this since the initial request was to analyze for C only. After these first results were reported from CCQM, all laboratories were requested reanalyze for the cations as well using the same voltage.

Our results for N in VN are within 1 to 2 % mass fraction of three other laboratories again including the XPS result. The mass fraction balance is not as serious in this sample, but we noted the presence of Ar in an energy dispersive

spectrum and the presence of what may be small impurities although CCQM claims that they are not present.

Future Plans: We plan to continue working with CCQM on this project as needed. It has demonstrated the difficulty of achieving agreement between laboratories in the quantitative deteernination of light elements, so we expect additional instructions will be forthcoming.

Reference:
Marinenko, R., ***An Approach to the Evaluation of Titanium Carbide Specimens for Microanalysis Standards***, Proc. Micros. & Microanal.Mtg. 2006, Chicago, Ill, Micros. & Microanal., **12**, Suppl. 2, Kotula, P. et. al., eds., Cambridge U. Press, Cambridge, UK, 876CD.

Composition in % Mass Fraction (1 σ Relative Uncertainty in % in Parentheses)						
	Ti in TiC	**C in TiC**	**Total**	**V in VN**	**N in VN**	**Total**
NIST Avg.	68.76(2.1)	21.98(2.5)	90.74	78.46(1.9)	19.57(3.5)	98.63
CCQM Range		21.98-32.8			15.3-26.4	
Nominal Comp.	79.95	20.05		78.43	21.57	